

PHOTOACOUSTIC SPECTROSCOPIC STUDY OF OPTICAL BAND GAP OF $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ SEMICONDUCTORS¹

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ABSTRACT

Using the photoacoustic spectroscopy (PAS) we have measured, for the first time, composition dependent optical absorption coefficient and band gap of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ semiconductor at room temperature. The band gap E_0 estimated from the PAS spectra varies nonlinearly with Be-concentration. The exchange interaction of electrons in conduction and valence bands, effects of polytypes, microstructures and mixed crystallization (zinc-blend and wurtzite structures) effect are considered for the analysis of the data. The observed exponential edge (Urbach's edge) can be considered as an internal Franz-Keldish effect arising from the charged impurity-generated and "frozen-in" optical phonon-generated fields. The phonon-assisted indirect transition at the band tail regions for some samples are also observed from the present studies.

KEY WORDS: indirect transition, photoacoustic spectroscopy, semiconductor, Zn-Be-Se.

1. INTRODUCTION

During the past decade a great deal of attention has been attributed to the study of semiconducting alloys of technological importance for several reasons. Semiconducting and structural properties, such as energy gap, the lattice parameter, etc. of these alloys can be varied in a controlled fashion by changing appropriately the mole fraction of the magnetic ions in the alloys as in non-magnetic semiconductors e.g., Zn-Se-Te etc. This aspect being particularly important in the use of monolithic semiconductor heterostructures where lattice matching is of obvious importance. Secondly, these materials are also of interest for their magnetic properties, e.g., spin-glass transition [1], antiferromagnetic cluster formation [2], magnon excitations [3] and other other magnetic effects of current interest. Thirdly the presence of magnetic ions in the lattice leads to spin-spin exchange interaction between the localized magnetic moments and the band electrons [4]. This interaction effects the energy band and impurity level parameters of these materials (e.g., by exchanging electronic g-factors), resulting in a new physical effect. Such novel and potentially important phenomena as the magnetic field-induced overlap between valence and conduction bands occurring in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ [5], extremely large Faraday rotation in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ [6], giant magnetoresistance associated with hopping conduction in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ [7] and the magnetic polaron observed in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ [8] are all consequences of the spin-spin exchange interaction.

To the best of our knowledge, no photoacoustic (PAS) investigation of the energy band structure, optical absorption coefficient etc. of many technologically important semiconducting materials has so far been made. These materials are very important for many of their applications in optical and electronic devices [9]. **The need to fine tune the band gaps of semiconducting alloys in various device applications** like light emitting diodes, low

loss optical fiber, heterojunction lasers, infra-red detector, solar cells etc., has provoked to understand the band gap variation in terms of properties of the constituent composition in the semiconducting alloy. Here we have studied the optical response of the semiconducting alloy $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ by photoacoustic spectroscopy which being a highly sophisticated and very sensitive technique for the nondestructive characterization of semiconductors and other materials [10]. The nonradiative transition processes which are associated with the band structure, defect related energy loss mechanism, etc. can be obtained directly and very accurately from the analysis of PAS spectra [11-13]. In this paper the main objective of the study are to find out the effect of Be substitution on the optical absorption and band gap at room temperature.

2. EXPERIMENTAL

For the preparation of the samples $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($x = 0.0, 0.086, 0.17, 0.26$), ZnSe and metallic Be (each of purity 99.99%) are used as starting materials. Desired amount of the mixture are ground to powder and pressed into thin pellets. These pellets are sealed in evacuated quartz tube and placed inside the furnace at about 1400 to 1500°C for several days. The ampoules were then furnace cooled at room temperature. The samples thus prepared were crystalline in nature and their composition and structure were tested by x-ray powder diffraction (Phillips:Model PW 1710) studies with $\text{CuK}\alpha$. The energy dispersive x-ray (EDX) experiment (Model KEVEV 3600-0388, USA) confirms the ratio of the constituent atoms within $\pm 2\%$.

The single beam photoacoustic spectrometer used in the present investigation consists of a PA cell containing the sensitive microphone, a 1000W Xe lamp with power supply

(Muller, type SVX 1000, Germany), monochromator (Oriel 77250), and a mechanical chopper (SR540) discussed elsewhere [13,15]. The PA signal produced is detected by a sensitive microphone (Bruel & Kjaer 4147) and processed by using a preamplifier and a lock-in-amplifier (SR530). To minimize the light scattering, very thin (~3-4 mm dia and ~0.3 mm thick) samples were used for the PAS studies. All the spectra were recorded at room temperature using the chopping frequency of 120Hz. The optical band gap is determined by measuring the variation of normalized PA signal intensity with the wavelength of the incident light. The PA spectrum obtained from highly absorbing carbon black powder was used to normalize the spectrum of the samples. An IBM personal computer was used for the acquisition and processing the data from the lock-in-amplifier through an RS232 interface.

3. RESULTS AND DISCUSSIONS

The normalized PA spectra of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($0 \leq x \leq 0.3$) as a function of incident wavelength is shown in Fig.1. The optical absorption coefficient α for thermally thick samples is calculated from the relation [16]

$$\alpha = (1/\mu_s)[q^2 + q(2-q^2)^{1/2}]/(1-q^2) \quad (1)$$

where q is the normalized PA amplitude and μ_s is the thermal diffusion length ($\sim 6.52 \times 10^{-3}$ cm). The variation of absorption coefficient of the samples with the incident photon energy is shown in Fig.2. The absorption spectrum of the Zn-Be-Se system consists of three distinct regions viz. high absorption region [$h\nu > E_o$ ($\alpha > 10^3 \text{ cm}^{-1}$)], the exponential region and the weak absorption tail. The absorption spectra shows that the transition is allowed and direct in nature

in quantum mechanical sense. In the high absorption region, the absorption coefficient α for the direct transition is governed by [17,18]

$$\alpha h\nu = A(h\nu - E_0)^{1/2} \quad (2)$$

where α is a constant. The direct transition in this system is confirmed from the plot of $(\alpha h\nu)^2$ vs $h\nu$ for various composition as shown in Figs.3a, b, c and d. The values of the corresponding optical band gap(E_0) are estimated (where the dotted lines meet the abscissa). It is found that the variation of E_0 with composition (x) is nonlinear in nature (Fig.3) obeys the relation $E_0(x) = 3.314x^2 + 0.67x + 2.618$. The variation is not very sharp and this might be due to the fact that mixed crystals $Zn_{1-x}Be_xSe$ crystallize [18] in zinc-blend structure for $x \leq 0.19$, in a mixture of zinc-blend and wurtzite structure for $0.19 \leq x \leq 0.3$. From the variation of absorption coefficient α with incident photon energy $h\nu$, the exponential edge (Urbach's edge) is also observed. The absorption coefficient in this region can be written as [17]

$$\alpha = \alpha_0 \exp [\gamma \{ h\nu - E_0(T) \} / k_B T^*] \quad \text{for } h\nu < E_0(T) \quad (3)$$

where α_0 and γ (order of magnitude is unity) are constant, $E_0(T)$ is temperature dependent band gap, and T^* is the effective temperature [19] which is almost constant below a critical value T_0 and is proportional to T at higher temperature region (above T_0). From Eq.(3) one also finds Urbach's rule viz. $d(\ln \alpha)/d(h\nu) = \gamma/k_B T^*$, which suggest that the sharp absorption edge becomes broader as the temperature rises above T_0 . This region is strongly related to the structural properties of the sample and can be correlated with impurity concentration of the sample [17]. Recently it has been shown [20-22] that $\gamma/k_B T^*$ is constant with temperature for polycrystalline materials.

The perturbation of the band edge may arise from intrinsic charged impurities as well as from the frozen-in optical phonon [23]. Such a perturbation may produce a local electric

field [17,23] which may be very large, $\sim 10^5$ V/cm. The relation between the local internal field and the Franz-Keldysh effect was shown by Redfield [24], Dow and Redfield [25,26]. They proposed that the fluctuation of the internal field is responsible for the exponential edge as observed in the present studies.

The tail in the absorption spectrum close to the band edge investigated from the PAS experiment (Fig.1) is associated with various factors such as phonon-assisted transition, purity and thermal history [27], and also on the thickness of the sample [24]. In this region ($h\nu < E_o$), the dependence of α on $h\nu$ obeys the following relation [23]

$$\alpha = B(h\nu - E_{oi} + E_p)^2 / \exp(E_p/k_B T - 1), \quad (4)$$

where B is a constant nearly independent of photon energy, T is the absolute temperature, and k_B is the Boltzmann constant, E_p and E_{oi} are, respectively, The phonon energy and optical energy gap for the indirect transition (E_p obtained from the extrapolation of the linear portion of $\alpha^{1/2}$ vs. $h\nu$ plot to the energy axis where $\alpha = 0$ (as shown in Fig.5a,b). The value of the phonon energy e_p is obtained from the above relation (Eq.4) following $E_p = (E_{oi} - h\nu)$ at $\alpha = 0$. For ZnSe, the phonon energies (E_p) are 75, 130, 180 meV corresponding to optical phonon wave numbers 601, 1040, 1440 cm^{-1} . For $\text{Zn}_{0.83}\text{Be}_{0.17}\text{Se}$ these phonon wave numbers are 201, 482, 803 cm^{-1} . For other samples no phonon assisted transition was observed.

4. CONCLUSION

From the PAS studies of the semiconducting alloys $\text{Zn}_{1-x}\text{Be}_x\text{Se}$, direct band to band transition is observed for absorption coefficient values greater than 10^3 cm^{-1} . The feature of the PAS data

enabled us to determine values of the fundamental band gap as a function of Be molar fraction x . The dependence of E_0 on x is nonlinear which might be due to the exchange interaction of electrons in conduction and valence bands with the s-electrons of Be ion interactions, effect of polytypes, micro structures and mixed crystallization (zinc-blend and wurtzite structures). These effects are yet to be clearly explained.

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REFERENCES

1. R. R. Galazka, "*Lecture notes on physics*" Vol.152.(Springer, Berlin. 1982), S. B. Oseroff *Phys. Rev.* **25**: 6584 (1982).
2. T. Dolling, T. M. Holden, V. F. Sears, J. K. Furdyna and W. Giriat, *J. Appl. Phys.* **53**: 7644 (1982).
3. A. K. Ramdas, *J. Appl. Phys.* **53**: 7649 (1982).
4. J. A. Gaj, *J. Phys. Soc. Japn.* **49** Supl. A: 797 (1980).
5. R. R. Galazka and J. Kossut in "*Lecture notes on physics*" Vol.32 (Springer, Berlin. 1980).
6. J. A. Gaj, R. R. Galazka and M. Nawrocki, *Solid State Commun.* **25**: 193 (1978).
7. A. Mycielski and J. Mycielski, *J. Phys. Soc. Japn.* **49**: 809 (1980).
8. M. Nawrocki, R. Planel, G. Fishman and R. R. Galazka, *Phys. Rev. Lett.* **46**: 735 (1981). *Solid State Commun.* **48**: 8453 (1983).
9. R. B. Bylsma, W. M. Becker, J. Kossut, U. Debska and D. Youdershort, *Phys. Rev.* **B31**: 795 (1985).
10. F. F. Morehead and G. Mandel, *Appl. Phys. Lett.* **5**: 53 (1964).
11. V. P. Zarove and V. S. Letokhov, "*Laser optoacoustic spectroscopy*", Springer Series in Optical Sciences, Vol. **37** (Springer, Berlin, 1986).
12. A. C. Tam, *Rev. Mod. Phys.*, **58**: 381 (1986).
13. B. K. Sarkar, S. Chatterjee, R. K. Mukherjee and B. K. Chaudhuri, *J. Mat. Sc. Lett.* **16**: 1499 (1997).
14. W. M. Becker in "*Diluted magnetic semiconductors*", ed. By J. K. Furdyna and J. Kossut; Semiconductors and semimetals series. Vol. **25** Academic, New York, 1988.

15. A. K. Gosh and B. K. Chaudhuri, J. Appl. Phys., **80**: 5292 (1996).
16. P. Poulet, J. Chambrn and R. Unterreiner, J. Appl. Phys. **51**: 1738 (1980).
17. J. I. Pankove, "*Optical processes in semiconductors*" (Dover, New York, 1975).
18. A. K. Arora and T. Sakuntala, Phys. Rev. **B52**: 11052 (1995).
19. H. Mahr, Phys. Rev. **132**: 1880 (1963).
20. L. Samuel, Y. Brada, A. Burger and M. Roth, Phys. Rev. **B36**: 116 (1987).
21. L. Samuel, Y. Brada and R. Beserman, Phys. Rev. **B37**: 4671 (1987).
22. M. Numann-Spallart, E. Galun, G. Hodes, C. Lavy-Clement, Y. Marfaing, E. Muranevich and r. Tenne, J. Appl. Phys. **73**: 7753 (1993).
23. Tauc, in "*Amorphous and liquid semiconductors*", edited by J. Taut, (Plenum, New york, 1974), "*The optical properties of solids*", edited by F. Abeles (North Holland, Amsterdam, 1970).
24. Redfield, Phys. Rev. **130**: 916 (1963).
25. J. D. Dow and R. Redfield, Phys. Rev. **B1**: 3358(1970). Phys. Rev. Lett. **6**: 762 (1971).
26. A. Vasco, D. Lezal and L. SRB, J. Non-cryst. Solids **4**: 311 (1970).
27. R. B. Bylsma, W. M. Becker, J. Kossut, U. Debska and D. Yodershort, Phys. Rev. **B33**: 18207 (1986).
28. F. Rys, J. S. Helman and W. Baltensperger, Phys. Condens. Mater, **6**: 105 (1967).
29. C. Hass, Phys. Rev. **B 168**: 531 (1968).

Figure Captions

Figure 1. Normalized photoacoustic (PA) spectra of four typical $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ system with (a) $x = 0.0$, (b) $x = 0.086$, (c) $x = 0.17$ and (d) $x = 0.26$ as a function of wavelength of incident light.

Figure 2. Variation of absorption coefficient of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ as a function of incident photon energy with (a) $x = 0.0$, (b) $x = 0.086$, (c) $x = 0.17$ and (d) $x = 0.26$.

Figure 3(a). Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ sample with $x = 0.0$.

(b) Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ sample with $x = 0.086$.

(c) Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ sample with $x = 0.17$.

(d) Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ sample with $x = 0.26$.

Figure 4. Variation of energy gap (estimated from Fig.3a, b, c and d) as a function of concentration (x).

Figure 5(a). Plot of $\alpha^{1/2}$ vs. $h\nu$ for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ sample with $x = 0$.

(b) Plot of $\alpha^{1/2}$ vs. $h\nu$ for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ sample with $x = 0.17$.

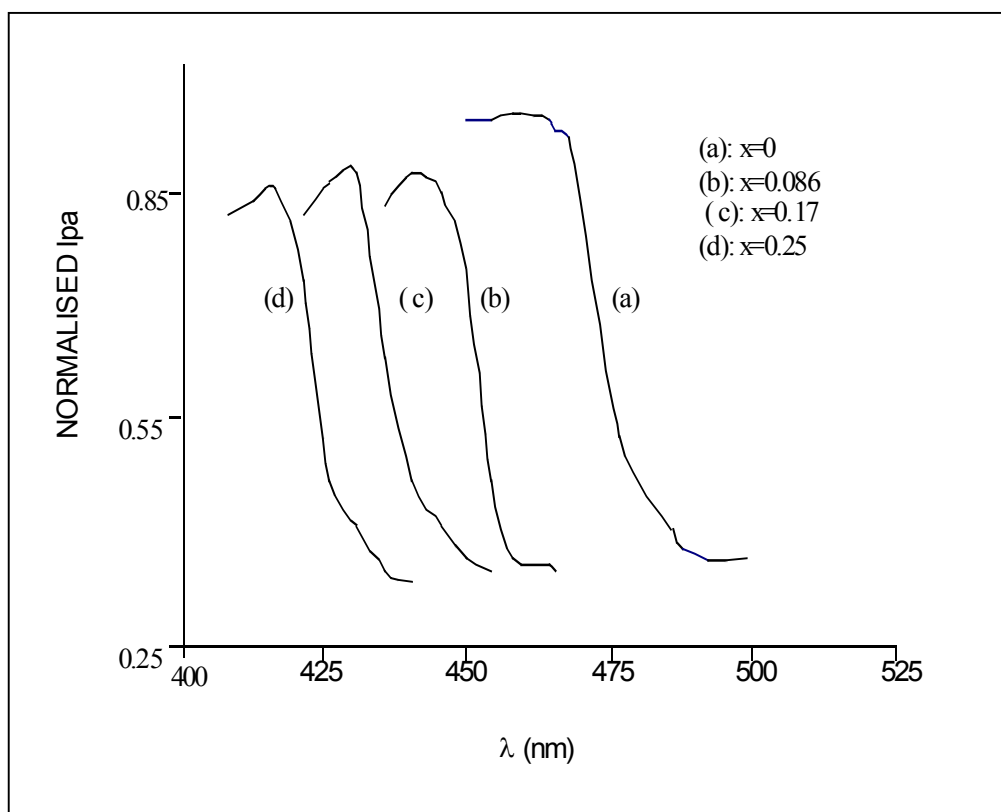


FIG-1

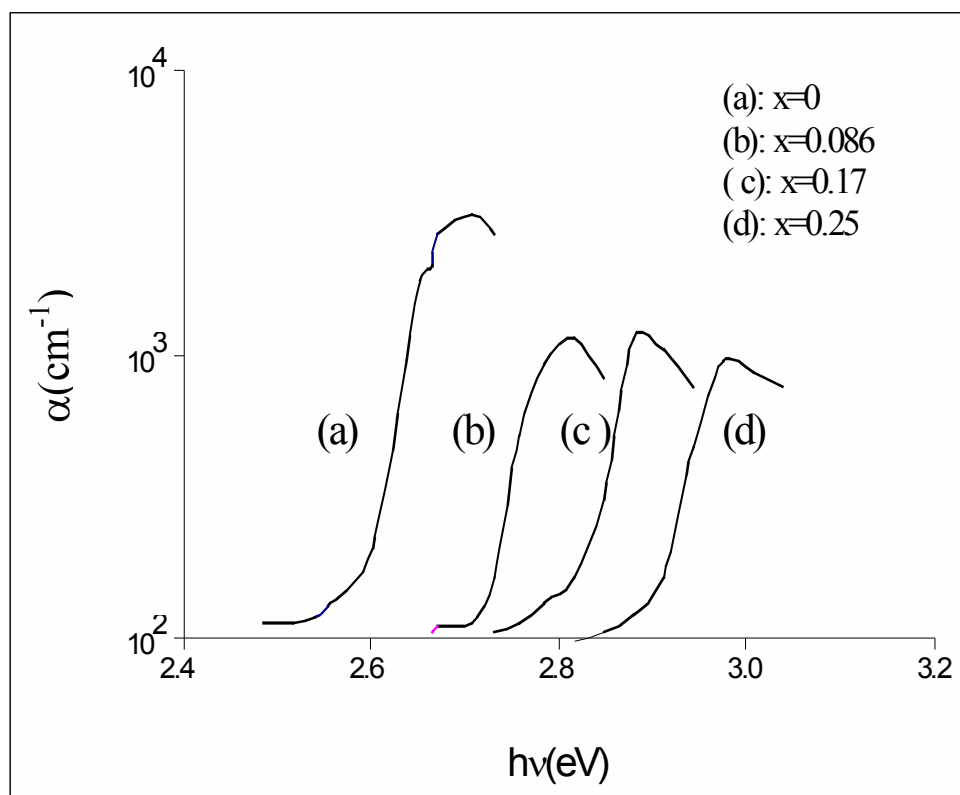


FIG-2

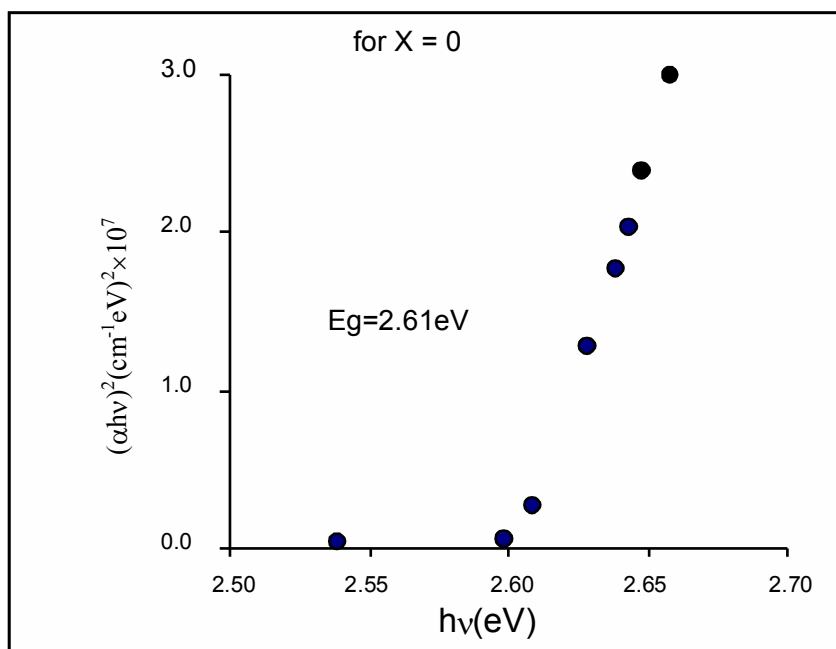


FIG-3(a)

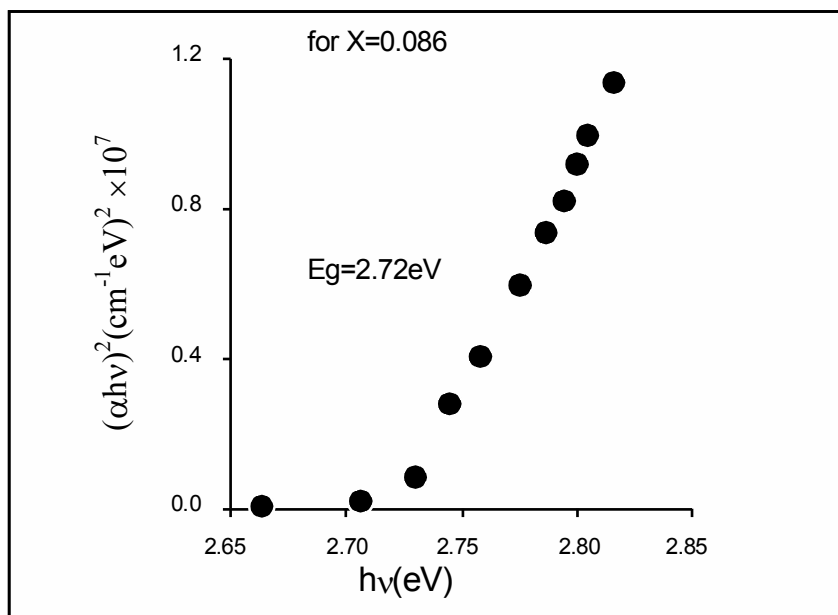


FIG-3(b)

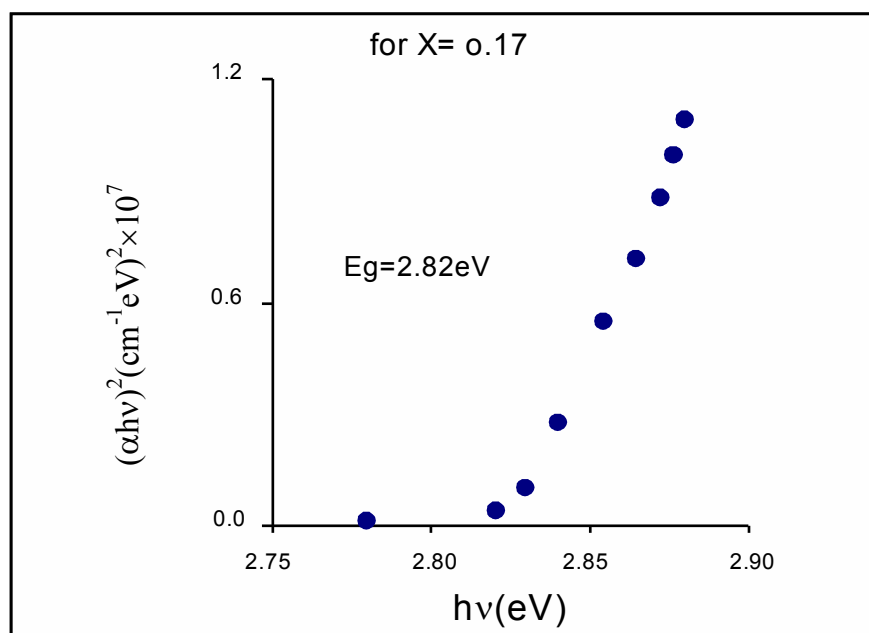


FIG-3(c)

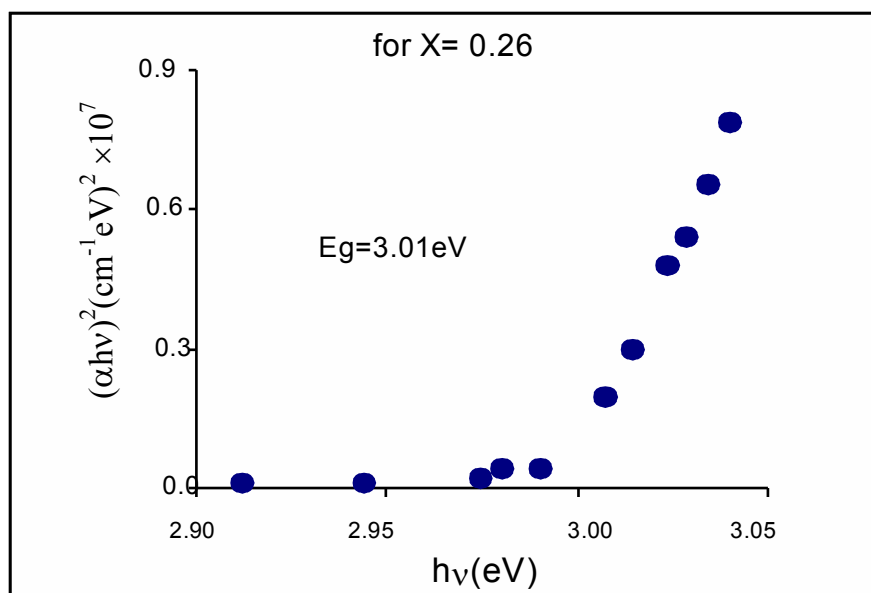


FIG-3(d)

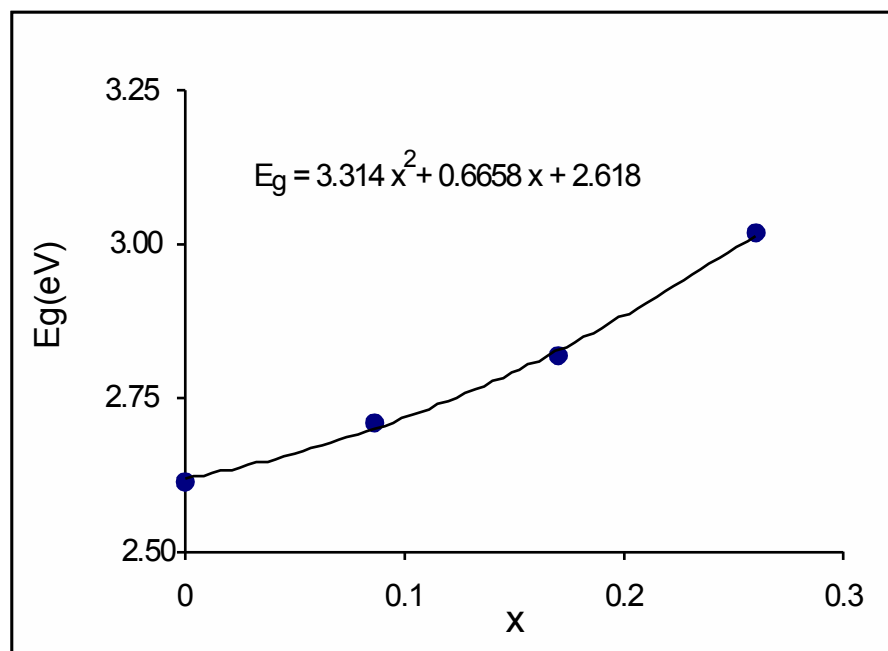


FIG-4

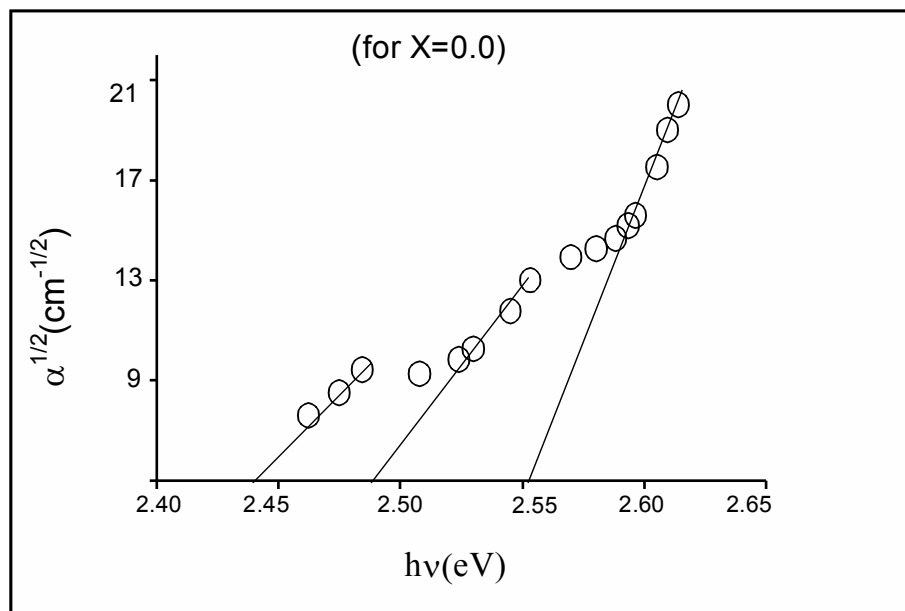


FIG-5(a)

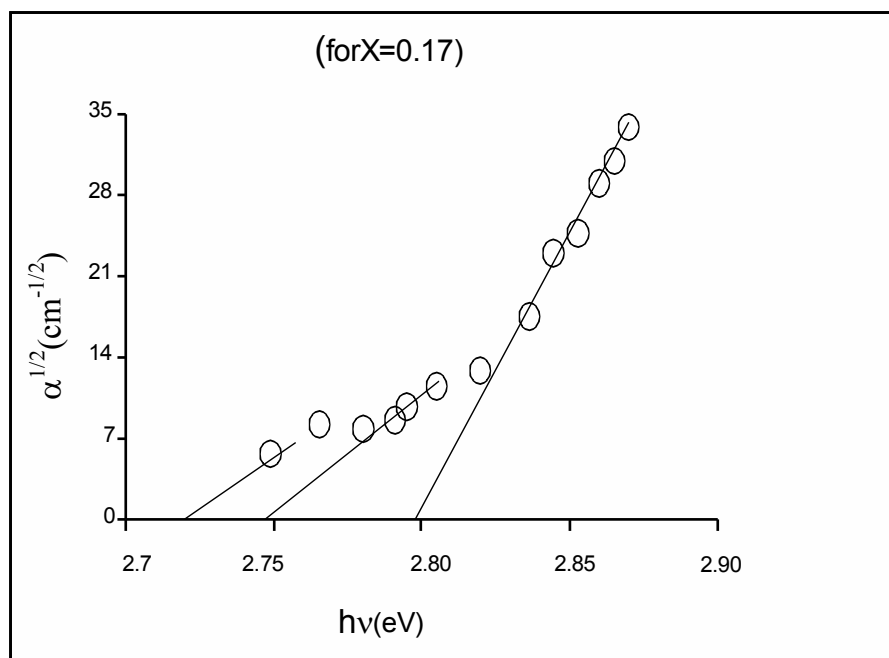


FIG-5(b)

